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tine much more fully. When munjistine is digested with moderately strong nitric acid, as already stated, copious fumes are given off, the munjistine gradually dissolving and forming a colourless solution. When this is evaporated to dryness on the water-bath, a white crystalline mass is obtained, consisting almost entirely of phthalic acid contaminated with a small quantity only of oxalic acid. The oxalic acid may be easily removed by washing the mass with a little cold water and then pressing between folds of bibulous paper, or by neutralizing the mixture of the two acids with lime and then treating with boiling water, which dissolves the phthalate of lime. The acid freed from oxalic acid by either of these methods presents all the usual reactions of phthalic acid. One of the most convenient ways of purifying it consists in subliming it repeatedly in a Mohr's apparatus, when the anhydrous acid is obtained in beautifully white iridescent four-sided prisms, frequently several inches in length. ·3745 grm. of the crystals of the anhydride, burnt with chromate of lead, gave ·891 grm. carbonic acid and ·095 grm. of water.

	Theory.	Expt.	Marignac.	Laurent.
C_{16}.... 96	64·86	64·89	64·88	64·70
H_4.... 4	2·70	2·81	2·71	2·38
O_6.... 48	32·44	32·30	32·41	32·92

From this result it is evident that the acid chiefly produced by the action of nitric acid upon munjistine is phthalic acid, which, as is well known, may also be procured from alizarine and purpurine. This reaction, therefore, indicates a very close relationship between these three substances, the only true colouring principles of madder with which we are at present acquainted.

VI. "Notes of Researches on the Poly-Ammonias.—No. XXIV. On Isomeric Diamines." By A. W. HOFMANN, LL.D., F.R.S. Received May 26, 1863.

In a former paper* I have described phenylene-diamine, an aromatic diamine which is formed by the action of powerful reducing agents upon dinitrobenzol. Phenylene-diamine, the last product of this reaction, is preceded by the formation of an intermediate compound, *nitraniline,* a substance discovered many years ago by Dr. Muspratt and myself[*],

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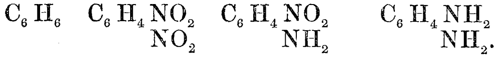
* Proc. Roy. Soc. vol. xi. p. 518.



$$\begin{array}{cccc} C_6H_6 & C_6H_4\begin{matrix}NO_2\\NO_2\end{matrix} & C_6H_4\begin{matrix}NO_2\\NH_2\end{matrix} & C_6H_4\begin{matrix}NH_2\\NH_2.\end{matrix} \end{array}$$

Benzol. Dinitrobenzol. Nitraniline. Phenylene-diamine.

Nitraniline, as might have been expected, was found to be readily convertible into phenylene-diamine.

By the researches of M. Arppe[†], chemists have become acquainted with a *second nitraniline,* which is obtained by the action of fuming nitric acid upon phenyl-pyrotartramide and subsequent treatment of the nitro-compound with potassa. This substance, which, as I afterwards found, may be more readily prepared by a similar treatment of other less difficultly obtainable phenylamides, such as phenyl-acetamide or phenyl-succinamide, is isomeric with ordinary nitraniline, but differs from the latter compound both in its physical and chemical properties, so as to leave no doubt regarding the individuality of the two compounds, which have accordingly been distinguished as *alpha-nitraniline* and *beta-nitraniline.* This singular isomerism, which has been traced also in other phenyl-derivatives, remains unexplained[‡]. Whilst engaged with the examination of phenylene-diamine, the idea naturally suggested itself, to ascertain whether beta-nitraniline, when submitted to reducing agents, would yield a body isomeric but differing from the phenylene-diamine obtained from dinitrobenzol and alpha-nitraniline.

Beta-nitraniline is readily reduced by a mixture of iron and acetic acid. The basic compound which distils over has the same composition as phenylene-diamine, viz. $C_6H_8N_2$, and presents in its properties many analogies with this substance, but it is far from being identical with it. The two diatomic bases obviously are related to each other in the same manner as the two nitranilines from which they are derived, and I propose therefore to distinguish them as *alpha-phenylene-diamine* and *beta-phenylene-diamine.* Beta-phenylene-diamine differs from alpha-phenylene-diamine by its superior crystallizing power: whilst the latter for days and often for weeks remains liquid, the former immediately, when separated from one of its salts by an alkali, solidifies into a beautifully crystalline mass. The fusing-point of alpha-phenylene-diamine is 63° (corr.), that of beta-phenylene-diamine is 140° (corr.); the former boils at 287° (corr.), the latter at 267° (corr.). Beta-phenylene-diamine is remarkable for the facility with which it sublimes even at temperatures below its boiling-point. The experiment succeeds particularly well in a current of hydrogen gas, when the base is obtained in splendid crystalline plates resembling pyrogallic acid.

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[*] Chem. Soc. Mem. vol. iii. p. 112.

[†] Chem. Soc. Journ. vol. viii. p. 175.

[‡] Among the various attempts I have made to decipher this isomerism, I may mention the treatment of the two nitranilines with the iodides of methyl and ethyl. But these substances are not acted upon by the reagents in question, and I take this opportunity of correcting an error which has crept into my paper on the molecular constitution of the volatile organic bases (Phil. Trans. 1850, vol. i. p. 93). In this paper I state that the action of iodide of ethyl on nitraniline gives rise to the formation of hydriodate of ethyl-nitraniline. This statement is based upon a single platinum determination. The platinum-salt of nitraniline contains 28·66 per cent. of platinum, that of ethyl-nitraniline 26·53 per cent. Analysis had furnished me 26·23 per cent. I have since satisfied myself that the salt was the imperfectly purified platinum-salt of nitraniline.

The salts of beta-phenylene-diamine, although they are more soluble than the corresponding alpha-phenylene-diamine salts, are distinguished by the same superior crystallizing power. They are all remarkable for the facility with which they yield beautiful and mostly well-formed crystals.

I have examined only two of these salts somewhat more minutely.

Hydrochlorate of Beta-phenylene-diamine.—This salt crystallizes in large prisms, which are at present in the hands of M. Quintino Sella. Extremely soluble in water, difficultly soluble in hydrochloric acid, it contains

$$C_6H_8N_2, 2HCl.$$

Hydrobromate of beta-phenylene-diamine resembles in every respect the hydrochlorate. The crystals, which were found to have the formula

$$C_6H_8N_2, 2HBr,$$

are apt to assume a reddish tint when left in contact with the air.

Platinum-salt.—Light-yellow plates extremely soluble in water and readily decomposed by heat. Composition:

$$C_6H_8N_2, 2HCl, 2PtCl.$$

The sulphate and nitrate are easily crystallizable salts, somewhat less soluble in water than the hydrochlorate.

Beta-phenylene-diamine and its salts are remarkable for the facility with which they are converted into violet- and blue-coloured compounds under the influence of oxidizing agents such as chlorine, bromine, chromic acid, ferric and platinic chloride, &c.

Both alpha- and beta-phenylene-diamine are readily attacked by the iodides of the alcohol radicals; and a means was thus afforded of ascertaining whether both substances exhibit the same degree of substitution. Since only the last products of substitution presented any interest, I have submitted the two bases to methylation. This experiment showed that both alpha- and beta-phenylene-diamine are capable of absorbing six equivalents of methyl to produce ammonium compounds of perfect substitution, and that both bases must therefore be represented by the formula

$$\left.\begin{matrix} C_6\,H_4 \\ H_2 \\ H_2 \end{matrix}\right\} N_2.$$

In the case of both bases, alternate treatment with iodide of methyl and oxide of silver or distillation with soda, thrice repeated, leads to the formation of a well-crystallized iodide of the formula

$$C_{12}\,H_{22}\,N_2\,I_2 = \left[\left.\begin{matrix} (C_6\,H_4)'' \\ (C\ H_3)_6 \end{matrix}\right\} N_2\right]'' I_2.$$

Whether prepared from alpha- or from beta-phenylene-diamine, this salt crystallizes in plates extremely soluble in water, less so in alcohol. I have found no other difference except that the beta-phenylene-compound is more soluble than the derivative of the alpha-base.

Whilst studying the methylated derivatives of the two bases, I have, of course, repeatedly obtained the lower, still volatile bases, which on this occasion were submitted to a few experiments.

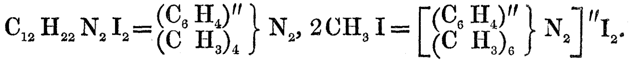
The compound

$$C_{10}\,H_{16}\,N_2 = \left.\begin{matrix} (C_6\,H_4)'' \\ (C\ H_3)_4 \end{matrix}\right\} N_2,$$

procured from beta-phenylene-diamine, when submitted to the action of iodide of methyl, was found to produce, in the first place, a rather difficultly soluble iodide,

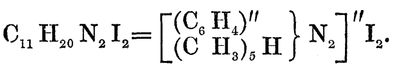
$$C_{11}\,H_{19}\,N_2\,I = \left.\begin{matrix} (C_6\,H_4)'' \\ (C\ H_3)_4 \end{matrix}\right\} N_2,\ CH_3\,I,$$

before it was converted into the final product



$$C_{12}H_{22}N_2I_2 = \left.\begin{matrix}(C_6H_4)''\\(C\ H_3)_4\end{matrix}\right\}N_2,\ 2CH_3I = \left[\left.\begin{matrix}(C_6H_4)''\\(C\ H_3)_6\end{matrix}\right\}N_2\right]''I_2.$$

The pentamethylated iodide, when treated with hydriodic acid instead of iodide of methyl, furnished the di-iodide of pentamethyl-phenylene-diammonium,



$$C_{11}H_{20}N_2I_2 = \left[\left.\begin{matrix}(C_6H_4)''\\(C\ H_3)_5H\end{matrix}\right\}N_2\right]''I_2.$$

The two phenylene-diamines are thus seen not only to be isomeric, but to have actually the same degree of substitution, as far as the latter may be rendered transparent by the action of iodide of methyl. Under these circumstances I was pleased to observe some additional phenomena which removed every doubt regarding their individuality.

On mixing a solution of beta-phenylene-diamine in sulphuric acid with peroxide of manganese, the odour of *kinone* becomes at once perceptible, and on heating the mixture, kinone distils over—the residuary liquid containing the sulphates of manganese and ammonium,

$$C_6H_8N_2 + 2H_2SO_4 + Mn_2O_2 = C_6H_4O_2 + Mn_2SO_4 + (H_4N)_2SO_4.$$

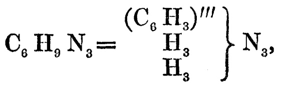
Beta-phenylene-diamine. Kinone.

The reaction proceeds with such ease that a few milligrammes of the diamine, when submitted to this treatment in the test-tube, yield a distinct crystalline sublimate of kinone, readily recognizable by its many salient properties. Alpha-phenylene-diamine, when similarly treated, evolves a faint odour of kinone, but does not yield crystals of this substance.

The elegant and easy formation of kinone in this reaction presents some interest, inasmuch as the process appears to be of general application, and will probably lead to the preparation of the higher homologues of kinone.

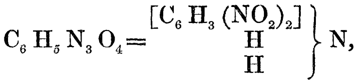
I have observed the formation of beta-phenylene-diamine in two additional reactions, which, in conclusion, I beg leave to mention.

In the hopes of obtaining the triamine of the phenyl-series



$$C_6H_9N_3 = \left.\begin{matrix}(C_6H_3)'''\\H_3\\H_3\end{matrix}\right\}N_3,$$

I submitted dinitrophenylamine,

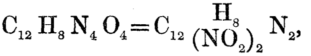


$$C_6H_5N_3O_4 = \left.\begin{matrix}[C_6H_3(NO_2)_2] \\ H \\ H\end{matrix}\right\} N,$$

to distillation with iron and acetic acid, but, instead of the compound which I endeavoured to procure, I invariably obtained beta-phenylene-diamine and ammonia,

$$\underbrace{C_6H_9N_3}_{\text{Phenylic triamine.}} + H_2 = \underbrace{C_6H_8N_2}_{\text{Beta-phenylene-diamine.}} + H_3N.$$

Again, dinitrazobenzol,



$$C_{12}H_8N_4O_4 = C_{12}\begin{matrix}H_8 \\ (NO_2)_2\end{matrix}N_2,$$

when submitted to the action of powerful reducing agents, yields likewise beta-phenylene-diamine

$$\underset{\text{Dinitrazobenzol.}}{C_{12}H_8N_4O_4} + 8H_2 = 4H_2O + \underset{\text{Beta-phenylene-diamine.}}{2C_6H_8N_2}.$$

Here also beta-phenylene-diamine is the final product of the reaction, the formation of which is preceded by that of another base, the *diphenine* of Messrs. Gerhardt and Laurent. Diphenine, according to these chemists, is

$$C_{12}H_{12}N_4,$$

a formula chiefly supported by the unequivocal presence of C_{12} in the molecule of azobenzol, $C_{12}H_{10}N_2$, whence it derives. The facility, however, with which diphenine under the influence of nascent hydrogen, by treatment with sulphuric acid and zinc, for instance, is converted into beta-phenylene-diamine renders it probable that the molecule of diphenine is

$$C_6H_6N_2,$$

when the two bases become related to each other as kinone and hydrokinone,

Kinone	$C_6H_4O_2$	Diphenine	$C_6H_6N_2$
Hydrokinone ..	$C_6H_6O_2$	Beta-phenylene-diamine	$C_6H_8N_2$.

I have hitherto vainly tried to transform kinone into diphenine or beta-phenylene-diamine; but it deserves to be noticed that M. Woskresensky*, by treating kinone with ammonia, has obtained a green beautifully crystalline mass, *kinonamide,* C_6H_5NO, which stands midway between kinone and diphenine,

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* Woskresensky, Journ. Pract. Chem. vol. xxxiv. p. 251.

$$\underset{\text{Kinone.}}{C_6H_4O_2}+H_3N=\underset{\text{Kinonamide.}}{C_6H_5NO}+H_2O.$$

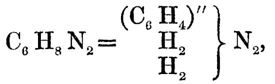
Another similar step of transformation would lead to diphenine,

$$\underset{\text{Kinonamide.}}{C_6H_5NO}+H_3N=\underset{\text{Diphenine.}}{C_6H_6N_2}+H_2O.$$

The preparation of azobenzol in large quantity, its transformation into dinitrazobenzol, and, lastly, the conversion by means of sulphide of potassium of the nitro-compound into diphenine, present so little difficulty, that treatment of diphenine with nascent hydrogen affords the easiest and simplest means of procuring beta-phenylene-diamine in appreciable quantity.

VII. "Contributions towards the History of the Colouring Matters derived from Aniline." By A. W. Hofmann, LL.D., F.R.S. Received June 2, 1863.

In a short paper recently submitted to the Royal Society, I pointed out the existence of two aromatic diamines, both represented by the formula



$$C_6H_8N_2=\left.\begin{matrix}(C_6H_4)''\\H_2\\H_2\end{matrix}\right\}N_2,$$

and closely resembling each other, but differing in some of their fundamental characters to such an extent that I did not hesitate to assert their individuality, and to distinguish them as alpha-phenylene-diamine and beta-phenylene-diamine.

The existence of two closely allied bodies among the diatomic derivatives of the phenyl-series very naturally suggested the idea of searching for two similarly related monatomic bases of the same group, and accordingly I undertook during the last week a careful comparison of specimens of aniline prepared by different processes. This comparative study is still incomplete, but I beg leave to record even now an observation which appears to merit the attention of chemists.

I have, in the first place, examined aniline obtained by distillation of isatin (indigo) with hydrate of potassium.

The base prepared in this manner boils at 182°, and possesses the general characters attributed to aniline. But neither by treatment